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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Industrial Application] This invention relates to amelioration of a nonaqueous electrolyte rechargeable battery, especially its electrolyte.

[0002]

[Description of the Prior Art] organic solvents, such as today, propylene carbonate, gamma-butyrolactone, dimethoxyethane, a tetrahydrofuran, and dioxolane, -- LiClO_4 , LiBF_4 , LiAsF_6 , LiPF_6 , and LiCF_3SO_3 etc. -- since the nonaqueous electrolyte cell which combined the electrolytic solution which melts a solute and is obtained, and the negative electrode which uses alkali metal, such as a lithium, as an active material has a high energy consistency, it came to be widely used for small electronic equipment including an electronic clock and a camera. One of the technical problems whose charge of this kind of nonaqueous electrolyte cell is enabled is that the gestalt of the alkali metal which deposits on a negative electrode in a charge process becomes the shape of arborescence and fibril, and the so-called dendrite [say / being needlelike]. When this dendrite grows remarkably, even if it makes it dissolve in the discharge process of about [that the danger of calling it the internal short circuit of a negative electrode and a positive electrode and ignition increases], and henceforth, the local dissolution of a dendrite advances, and since a part separates from a plate electrically, it can begin to melt no dendrites. That is, a cycle life becomes short, while the amount of discharge (dissolution) to the amount of charge (deposit) becomes small and charge-and-discharge effectiveness falls. The attempt added to the electrolytic solution as such an approach of solving a technical problem by using the ring compound containing two or more ketone groups as an additive occurs (JP,5-82168,A news).

[0003]

[Problem(s) to be Solved by the Invention] By the cell using the ring compound containing the two or more above-mentioned ketone groups, for example, a maleic anhydride, the succinic anhydride, etc. as an additive, when overdischarge of the cell was carried out to about 0V, it became clear that cell voltage produced un-arranging [that go up rapidly, and cannot fully charge a cell, but charge-and-discharge capacity decreases extremely in subsequent charge-and-discharge cycles] in early stages of the following charge process. It is because the ring compound containing two or more ketone groups has a large distortion because of the electronic repulsion between ketone groups, and cyclic structure and the reduction decomposition of this reason is easy to be carried out with the alkali metal which is a negative-electrode active material electrochemically. On the other hand, this compound exists in stability by the open circuit condition of a cell by mixing with carbonates, such as propylene carbonate. This is because the reaction of the ring compound and alkali metal with which carbonates, such as propylene carbonate, react easily with alkali metal, such as a lithium, and they contain two or more ketone groups is controlled as a matter of fact. However, in the closed circuit condition of a cell, the ring compound containing activity alkali-metal front face and two ketone groups or more contacts with use of a cell, reduction decomposition is carried out and a ring compound forms a firm coat on a negative-electrode front face. The thickness of the coat at this time is deposited increasingly, and becomes firm, so that overdischarge of the cell is carried out. Therefore, even if it is going to charge a cell after overdischarge, it becomes less easy to destroy a coat and it becomes difficult for the electrical potential difference in early stages of charge to rise rapidly, and to charge in the stable range at the electrochemistry target of the electrolytic solution. This invention aims at offering a nonaqueous electrolyte rechargeable battery with large dependability with a long charge-and-discharge cycle life with little cycle capacity degradation by obtaining the electrolytic solution which can charge even after removing such a conventional fault and performing overdischarge of a cell.

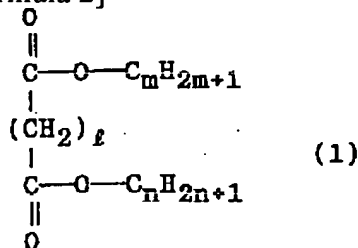
[0004]

[Means for Solving the Problem] The nonaqueous electrolyte rechargeable battery of this invention possesses a positive

electrode, the nonaqueous electrolyte of alkali ion conductivity, and the negative electrode that uses alkali metal as an active material, and said electrolyte contains the aliphatic series saturation dicarboxylic acid ester shown by the following formulas (1). Especially the desirable content of aliphatic series saturation dicarboxylic acid ester is more than 5 vol% among a solvent. Here, as for the main solvent of said electrolyte, it is desirable that it is at least one sort chosen from the group which consists of ethylene carbonate, propylene carbonate, and diethyl carbonate. Moreover, as for especially these main solvents, it is desirable among a solvent that it is more than 60 vol%.

[0005]

[Formula 2]



(ただし、 $\ell \geq 0$ 、 $m \geq 1$ 、 $n \geq 1$

である。)

[0006]

[Function] According to the place which this invention persons considered variously, for the straight chain structure, an aliphatic series saturation dicarboxylic acid ester compound has the small electronic repulsion between ketone groups, and does not have distortion originating in cyclic structure, either. Therefore, even if it contacts an activity alkali metal in the state of overdischarge, the frequency where electrochemical reduction decomposition called the electronic transition from alkali metal to a ketone group breaks out decreases. Moreover, an aliphatic series saturation dicarboxylic acid ester compound is mixing with carbonates, such as ethylene carbonate, propylene carbonate, and diethyl carbonate, an electrochemical reduction decomposition reaction is controlled further, and even if it changes a cell into an overdischarge condition, subsequent charge-and-discharge cycle lives are kept good.

[0007]

[Example] Hereafter, the example of this invention is explained. In addition, all examples were performed under the argon gas ambient atmosphere.

[Example 1] ethylene carbonate and propylene carbonate were mixed at a rate of 1:1 by the volume ratio, LiClO₄ was dissolved in this mixed solvent at a rate of one mol/l., and the electrolytic solution was prepared. Adipic-acid dimethyl was added at a 10 vol% rate to this electrolytic solution. Thus, the flat cell as shown in drawing 1 using the prepared electrolytic solution was constituted. Hereafter, it explains based on drawing 1. A positive electrode 1 is LiMn 2O₄. Powder, carbon black, and polytetrafluoroethylene powder were mixed, and pressurization molding was carried out at the positive-electrode can 3 which carried out spot welding of the expanded metal charge collector 2 of titanium. The negative electrode 4 stuck by pressure the lithium sheet pierced to disc-like to the obturation plate 6 which carried out spot welding of the expanded metal 5 of nickel. In the separator 7, the flat cell was constituted after pouring in the aforementioned electrolytic solution combining the positive-electrode can 3 and the obturation plate 6 through the gasket 8 using the porous membrane made from polypropylene.

the mixed solvent of the volume ratio 1:1 of [example 1 of comparison] propylene carbonate, and ethylene carbonate -- LiClO₄ -- the one mol [l.] electrolytic solution which came out comparatively and dissolved -- a maleic anhydride -- 10 vol% -- what was added was used and also the cell was constituted like the example 1.

[0008] In 25 degrees C, the charge-and-discharge cycle was repeated for the cell of the example 1 constituted as mentioned above and the example 1 of a comparison on condition that the current density of 2 mA/cm², discharge minimum electrical-potential-difference 2.0V, and charge upper limit electrical-potential-difference 3.5V, constant-resistance discharge was performed by 1kohm at the time of the 10th discharge, and it was left as it is for one month.

Drawing 2 draws the charging curve in 2 mA/cm² of the cell immediately after neglect, and drawing 3 plots the discharge capacity in each cycle of a cell. From these drawings, the rapid rise of cell voltage [in / in the cell of an example 1 / the charge first stage immediately after overdischarge] is not seen. On the other hand, it understands that the cell of the example 1 of a comparison is controlled by the charge upper limit threshold for the rapid rise of an electrical potential difference, and it becomes impossible to fully charge.

[0009] 1 and 3-dioxolane was used instead of the mixed solvent of ethylene carbonate and propylene carbonate used in the [example 2] example 1. LiClO_4 was dissolved in this solvent at a rate of one mol/l., adipic-acid dimethyl was added at a 10 vol% rate to this electrolytic solution, and also the flat cell was constituted like the example 1. In 25 degrees C, the charge-and-discharge cycle was repeated for this cell on condition that the current density of 2 mA/cm², discharge minimum electrical-potential-difference 2.0V, and charge upper limit electrical-potential-difference 3.5V, overdischarge was performed by constant resistance of 1kohm at the time of the 10th discharge, and it was left for one month. Drawing 4 plots the discharge capacity before and behind overdischarge. Moreover, the property of the cell of an example 1 of having used the mixed solvent of ethylene carbonate and propylene carbonate for the solvent was also plotted for the comparison. Drawing 4 shows that the discharge capacity in the charge-and-discharge cycle after overdischarge decreases a little compared with the case where the mixed solvent of ethylene carbonate and propylene carbonate is used, when dioxolane is used as a main solvent. This is because formation of the protective film by the reaction of dioxolane and a lithium negative electrode is slow, therefore reduction decomposition of the adipic-acid dimethyl comes to be carried out.

[0010] The flat cell was produced like the [example 3] example 1, using the mixed solvent of ethylene carbonate and propylene carbonate as a main solvent of the electrolytic solution. various kinds of dimethyl ester as shown in Table 1 as aliphatic series dicarboxylic acid ester added to the electrolytic solution -- 5vol(s)% -- it added. Thus, it asked for the number of cycles (cycle life) until it repeats a charge-and-discharge cycle on condition that the current density of 2 mA/cm², discharge minimum electrical-potential-difference 2.0V, and charge upper limit electrical-potential-difference 3.5V and discharge capacity becomes half [of 1 cycle eye] in 25 degrees C about the produced cell. Table 1 summarized the cycle life of the cell of the example of this invention, and also indicated the cycle life when not adding dimethyl ester for a comparison. Table 1 shows that the cell using the electrolytic solution which added aliphatic series saturation dicarboxylic acid ester improves as compared with the case where the cycle life is not added, and it is especially effective with the ester compound in the principal chain carbon number more than glutaric-acid dimethyl.

[0011]

[Table 1]

番号	$\begin{array}{c} \text{CH}_3\text{-O-C-(CH}_2\text{)}_l\text{-C-O-CH}_3 \\ \parallel \quad \parallel \\ \text{O} \quad \text{O} \end{array}$	サイクル寿命
1	$l = 0$; シュウ酸ジメチル	1 5 4
2	$l = 1$; マロン酸ジメチル	1 7 3
3	$l = 2$; コハク酸ジメチル	2 5 1
4	$l = 3$; グルタル酸ジメチル	3 0 2
5	$l = 4$; アジピン酸ジメチル	3 1 4
6	$l = 5$; ピメリン酸ジメチル	8 1 5
7	$l = 6$; スベリン酸ジメチル	3 0 6
8	$l = 7$; アゼライン酸ジメチル	3 0 3
9	$l = 8$; セバシン酸ジメチル	8 0 4
比較例	添加剤なし	1 3 8

[0012] Using diethyl carbonate as a main solvent of the [example 4] electrolytic solution, LiClO_4 was dissolved at a rate of one mol/l., and the electrolytic solution was prepared. various kinds of dialkyl adipate ester as shown in this

electrolytic solution in Table 2 -- 10 vol% -- it added. Thus, using the prepared electrolytic solution, the same flat cell as an example 1 was produced, the charge-and-discharge cycle was repeated on condition that the current density of 2 mA/cm², discharge minimum electrical-potential-difference 2.0V, and charge upper limit electrical-potential-difference 3.5V, and it asked for the number of cycles (cycle life) until discharge capacity becomes half [of 1 cycle eye]. Table 2 summarizes the cycle life of the cell of the example of this invention. When the alkyl group in which the alkyl group combined with an ester group has the carbon number of the die length more than an ethyl group from Table 2 is used, it turns out that especially a cycle life is extended.

[0013]

[Table 2]

番号	$\begin{array}{c} \text{C}_m\text{H}_{2m+1}-\text{O}-\text{C}-(\text{CH}_2)_4-\text{C}-\text{O}-\text{C}_m\text{H}_{2m+1} \\ \parallel \qquad \qquad \parallel \\ \text{O} \qquad \qquad \text{O} \end{array}$	サイクル寿命
1	m = 1 ; アジピン酸ジメチル	3 1 4
2	m = 2 ; アジピン酸ジエチル	3 5 5
3	m = 3 ; アジピン酸ジプロピル	3 7 2
4	m = 4 ; アジピン酸ジブチル	3 8 8
5	m = 5 ; アジピン酸ジペンチル	3 5 3

[0014]

[Effect of the Invention] As mentioned above, according to this invention, even if it performs overdischarge, a nonaqueous electrolyte rechargeable battery with the large long dependability of a cycle life is obtained small [capacity degradation].

[Translation done.]

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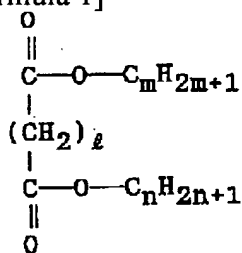
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CLAIMS

[Claim(s)]

[Claim 1] It is the nonaqueous electrolyte rechargeable battery which possesses a positive electrode, the nonaqueous electrolyte of alkali ion conductivity, and the negative electrode that uses alkali metal as an active material, and is characterized by said electrolyte containing the aliphatic series saturation dicarboxylic acid ester shown by ** 1.

[Formula 1]



(ただし、 $\ell \geq 0$ 、 $m \geq 1$ 、 $n \geq 1$

である。)

[Claim 2] The nonaqueous electrolyte rechargeable battery according to claim 1 which is at least one sort chosen from the group which the main solvent of said electrolyte becomes from ethylene carbonate, propylene carbonate, and diethyl carbonate.

[Translation done.]